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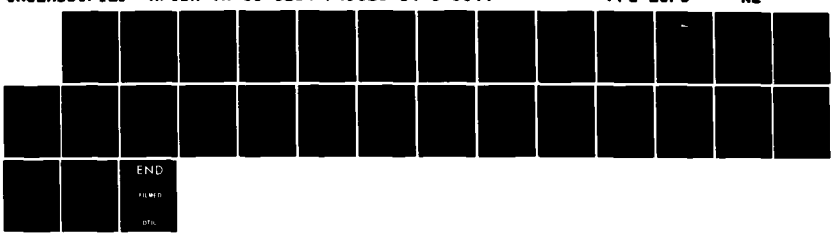

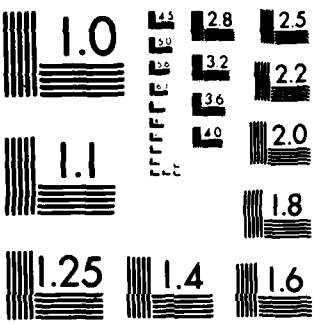

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EXPERIMENTAL STUDY OF DISSOCIATIVE ATTACHMENT IN OPTICALLY–PUMPED LITHIUM MOLECULES

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The first experimental observations of dissociative attachment in lithium dimmer molecules are presented. Lithium molecules are optically pumped via the $Li_2(B)$ electronic state into selected levels of the ground electronic state. Low energy electrons are created by two-step laser photoionization of lithium atoms. Product Li ions are detected by time-of-flight spectrometry. Preliminary analysis of the data gives a rate constant of 3.10^{-8} cm^3 sec^{-1} for the attachment of 0.1 eV electrons to lithium vibrational

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states v = 8 to v = 12, without strong dependence on the selected state.

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1.0 REVIEW OF PROGRAM TO DATE

1.1 SUMMARY

This program has been active in two phases, the first during 1982-83 and the second in 1984. During the first phase a new lithium supersonic nozzle apparatus was constructed and tested. The lithium beam density distribution was investigated, and tunable laser spectroscopy was used to measure the rotational temperature of the lithium dimers in the beam. Since the aim of the research was to measure attachment rates in optically pumped lithium molecules, a measurement was made to show the effectiveness of the pumping. Also the three-step ionization of Li atoms was used as a source of electrons for attachment. In the first phase the ions (positive or negative) were collected on a charge amplifier, which limited the experimental resolution of attachment and prevented the definite observation of Li^- signals. In that phase an upper bound on the attachment rate constant of $k_{DA} < 1 \times 10^{-8}$ cm^3 sec^{-1} was determined, for attachment to vibrational states $v'' \sim 13$ in the dimer molecule ground state $Li_2(X)$. This work is reported in detail in the first annual report[1] and also was presented at a symposium.[2]

Between the first phase and the second phase an investigation was performed, under corporate funding, of the two-step ionization of Li_2 molecules via the $Li_2(B)$ state. The purpose of this was to investigate autoionizing channels in Li_2 as possible routes to electron production in this experiment. A wealth of molecular Rydberg states were revealed, and analyzed for

the first time[3] to give new information about the molecular properties of the Li_2^+ ground state. This work explained certain puzzling intensity features which had been observed during the temperature measurement in Phase I.

In the second phase the experiment was improved in two principal ways: a lower electron temperature was used, which enhanced the interaction time with pumped molecules by slowing down the plasma expansion; and, more importantly, a channeltron detector was installed which could count individual ions. The use of this detector allowed time-of-flight resolution of the negative ions and revealed that a negative bias signal observed in the Phase I experiment in fact consisted of H^- and heavier negative ions such as OH^-. During the second phase a Li^- signal was observed which depended on optical pumping and had the correct time dependence for an attachment process. Preliminary analysis of the data revealed that the rate constant for dissociative attachment to states between v" = 7 and v" = 12 was $k_{DA} \sim 3 \times 10^{-8}$ cm^3 sec^{-1}, without any strong dependence on initial vibrational state.

In addition to the Li^- signal which depended on $Li_2(B-X)$ optical pumping, there was a slightly smaller signal which was present in the presence of the photoionization pulse alone, but which also was due to attachment as evidenced by its time dependence. Further work is needed to show whether this latter signal is due to optical pumping on the $Li_2(A-X)$ (v" = 5, v" = 1) band which is excited by exactly the Li atomic resonance wavelength of 671 nm, used for photoionization, or whether it is due to vibrationally excited dimers (in the v" > 10 region) formed by three-body recombination of Li atoms downstream of the nozzle. The state of the downstream dimers will be discussed in more detail below, as it is one of the subjects proposed for research in a program continuation.

In the second phase of the program, therefore, a proof of principle was established that optical pumping could be used to obtain very high rate constants for attachment in lithium - sufficiently high to be the basis of a new type of continuously operating Li^- source. Interesting light was also shed on the probable disposition of the Li_2^- potential energy curve which acts as a channel for attachment, in that the lack of strong dependence on vibrational state was consistent with a bound Li_2^- curve, as predicted by several recent calculations.

In the following subsections a more detailed discussion of the Li^- second phase observations is given. The measurements are far from complete and their completion is one of the subjects of a continuation proposal. Apart from this, and the beam dimer state distribution mentioned above, the other main concern for continued work will be the exploration of attachment at the higher electron densities needed in a real source, to assess whether any deleterious mechanisms come into play.

1.2 DETAILS OF THE 1984 ATTACHMENT MEASUREMENTS

1.2.1 Use of Two-Step Photoionization of Li

In the first phase a three-step photoionization of Li atoms was used[1] which involved excitation via the route

$$Li(2s\ ^2S_{1/2}) \rightarrow Li(2p\ ^2P_{1/2,3/2}) \rightarrow Li(3d\ ^2D_{3/2,5/2}) \rightarrow Li^+(^1S_0) + e^- \ (0.55\ eV)$$

The resulting electrons were calculated to rapidly thermalize into a Maxwellian distribution, followed by expansion of the Li^+, e^- plasma column on a timescale of ~ 0.5 μsec. This expansion was a limitation on the interaction time for attachment, during which the electron cloud overlapped the

region of optical pumping of Li_2. In order to increase the interaction time and simultaneously to increase the number of available electrons a change was made to the method of photoionization. The nitrogen laser photons were used directly to ionize the $Li(^2P_{1/2,3/2})$ level as shown in Figure 1. This second step had an estimated cross section of $\sim 1 \times 10^{-17}$ cm^2,(5) about three times less than that out of the ^2D level, but the nitrogen laser 337 nm output of a few mJ was 20 to 50 times greater than the 610 nm dye laser output used formerly for the third step. Unfortunately the N_2 laser beam divergence was rather poor, so that even using one of the N_2 lasers as an injector for a second one, the number of electrons produced per pulse was only slightly more than in the three-step case. The principal advantage of the two-step route was the much lower average electron energy of 0.13 eV, which gave an estimated expansion time of(1)

$$\tau_{ex} = r_{eo} \sqrt{\frac{m_i}{2\epsilon_o}} \sim 1.0 \times 10^{-6} \text{sec}$$

where r_{eo} is the initial 1/e radius of the charge cloud ($\sim$ 0.2 cm), m_i is the ion mass (Li^+) and ϵ_o is the initial electron energy (0.13 eV). Generally the optical pumping region was larger than the initial charge cloud, so that expanding electrons still had an opportunity to attach for several microseconds.

While the use of a decreased electron energy was helpful in that it extended the interaction time, it also may have had the effect of increasing the attachment cross section because of a feature of the Li_2^- energy level

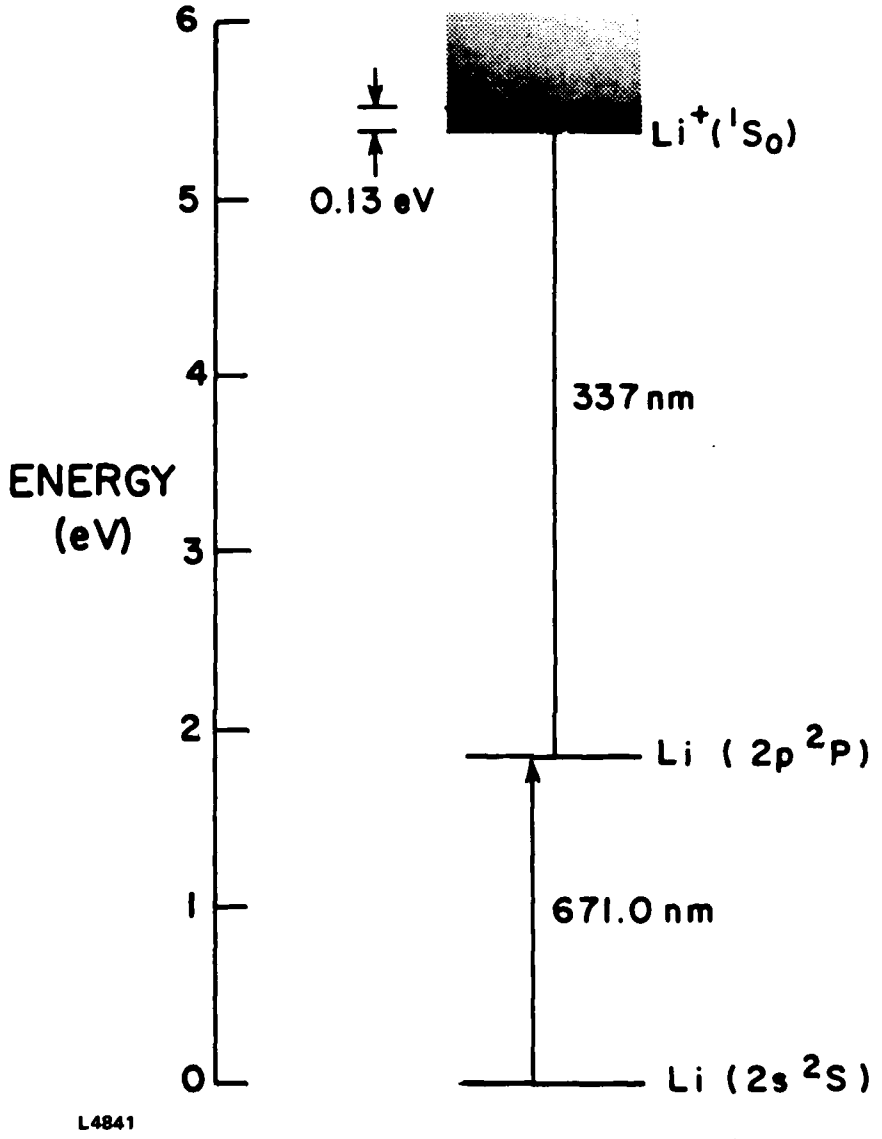


Figure 1 Illustration of the Two-Step Photoionization of Lithium Atoms

structure[6] which probably exists at low energy (~ 0.5 eV), namely an extremely strong shape resonance. Such a resonance might be a route to vibrational de-excitation of vibrationally excited Li_2 states, and could cause the electron energy distribution function to spread through inelastic and superelastic processes. In order to further study this possibility it will be proposed that tunable photoelectrons be used in the second part of the continuation.

In summary, the two-step photoionization that was used created ~ 1×10^{10} electron-ion pairs per cm^3 in a column of length 3 cm and thickness ~ 0.4 cm. Although these figures are comparable to those of the first phase, the much cooler electrons (0.13 eV as compared to 0.55 eV) allowed a longer interaction time for attachment, and may have avoided a troublesome shape resonance which could compete with attachment.

1.2.2 Introduction of a Channeltron Ion Detector

In Phase I the ions had been collected on a plate connected to a sensitive charge amplifier. The principal reason for this choice was that in an attachment measurement the sensitivity of a collector plate (with suitable bias grids) was guaranteed to be more or less equal for positive and negative ions, whereas there had been some room for doubt about the relative sensitivity of a channel electron multiplier, or channeltron, for the two species.

Fortunately the sensitivity of a channeltron was found[7] to be much the same for H^+ and H^- ions in the 1 keV energy range, and a similar result was stated to hold for deuterons. The 1.1 keV energy of our Li^+/Li^- extracted ions (half the 2.2 keV extraction potential difference), although representing only ~ 0.4 keV per unit of nuclear charge, would probably also

guarantee an equal sensitivity to Li^+ and Li^-. The apparent lack of data on this question is responsible for one of the uncertainties in the estimation of the attachment rate constant. The relative sensitivity notwithstanding, the very high sensitivity of a channeltron (single ions can be counted) makes its use very attractive.

We installed a Galileo 4800 series channeltron behind a 0.6 cm dia. hole in our previous charge collector plate at the end of the flight tube (Figure 2). The collector plate was kept for the purpose of comparison with our previous data. The channeltron was calibrated by reducing the Li^+ signal to low values and monitoring single ion counts. The correlation of the count rate with the collected charge gave the charge amplification of the channeltron at certain voltages. The relative channeltron gain was obtained at nearby voltages using larger ion signals (effective averaging of count rate), and a calibration curve built up (Figure 3) which agreed with the manufacturer's data to within 20 percent. An additional pair of deflector plates was installed at the channeltron entrance to suppress low energy electrons scattered from the region of the electron dump in the honeycomb structure. A 100 Vdc bias was always applied to these plates.

The channeltron was used in conjunction with a Biomation analyzer, which stored the charge collected in 1024 time intervals spread typically over a 5 μsec interval. This data was collected during several seconds of laser operation at 60 Hz, with chopping applied to the Li_2 (B-X) optical pumping, both with and without the ionization lasers, so that background effects could be subtracted and the signal dependence on pumping studied.

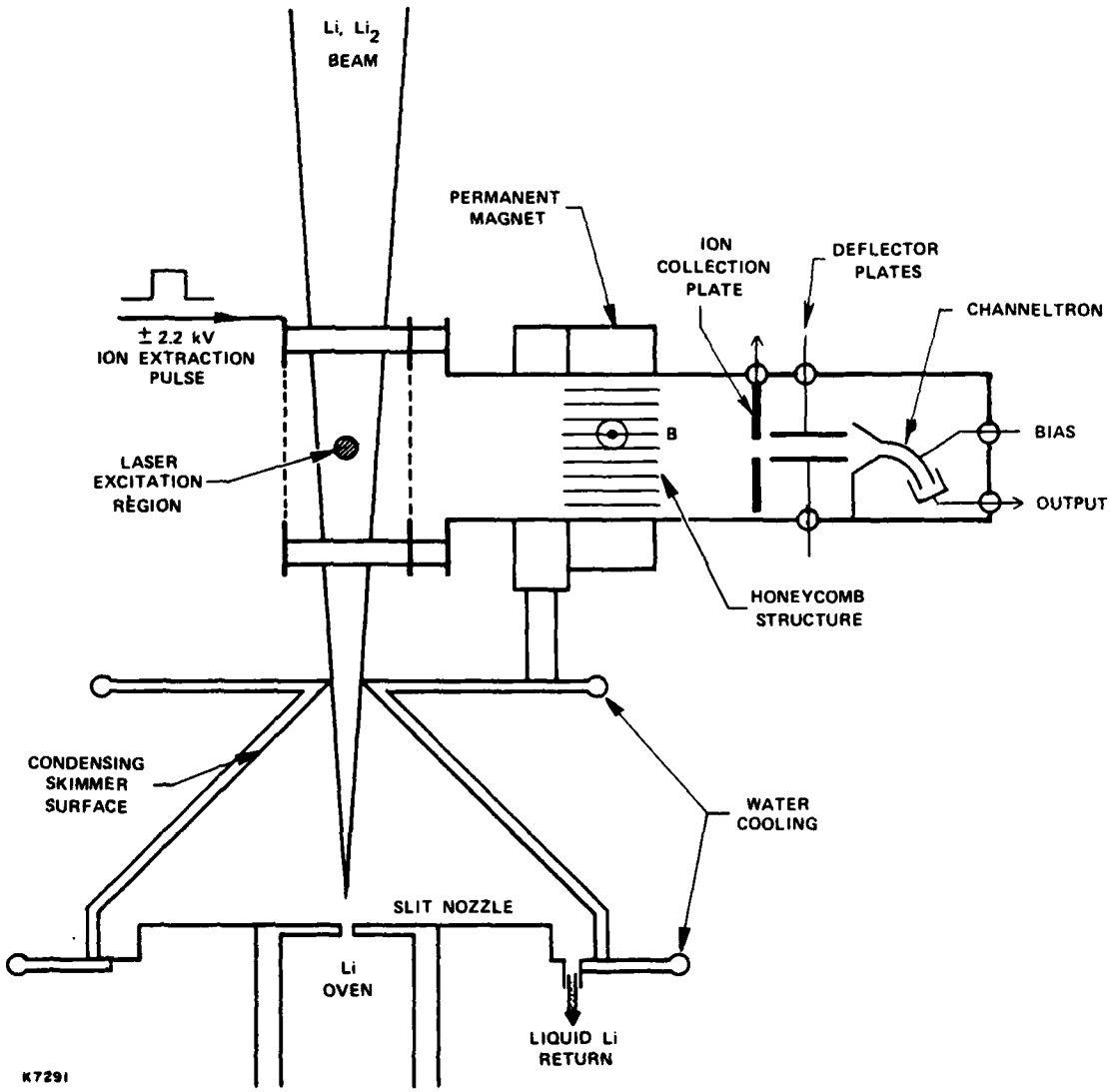


Figure 2 Sketch of the Experimental Arrangement for Optical Excitation, Ion Extraction and Ion Detection.

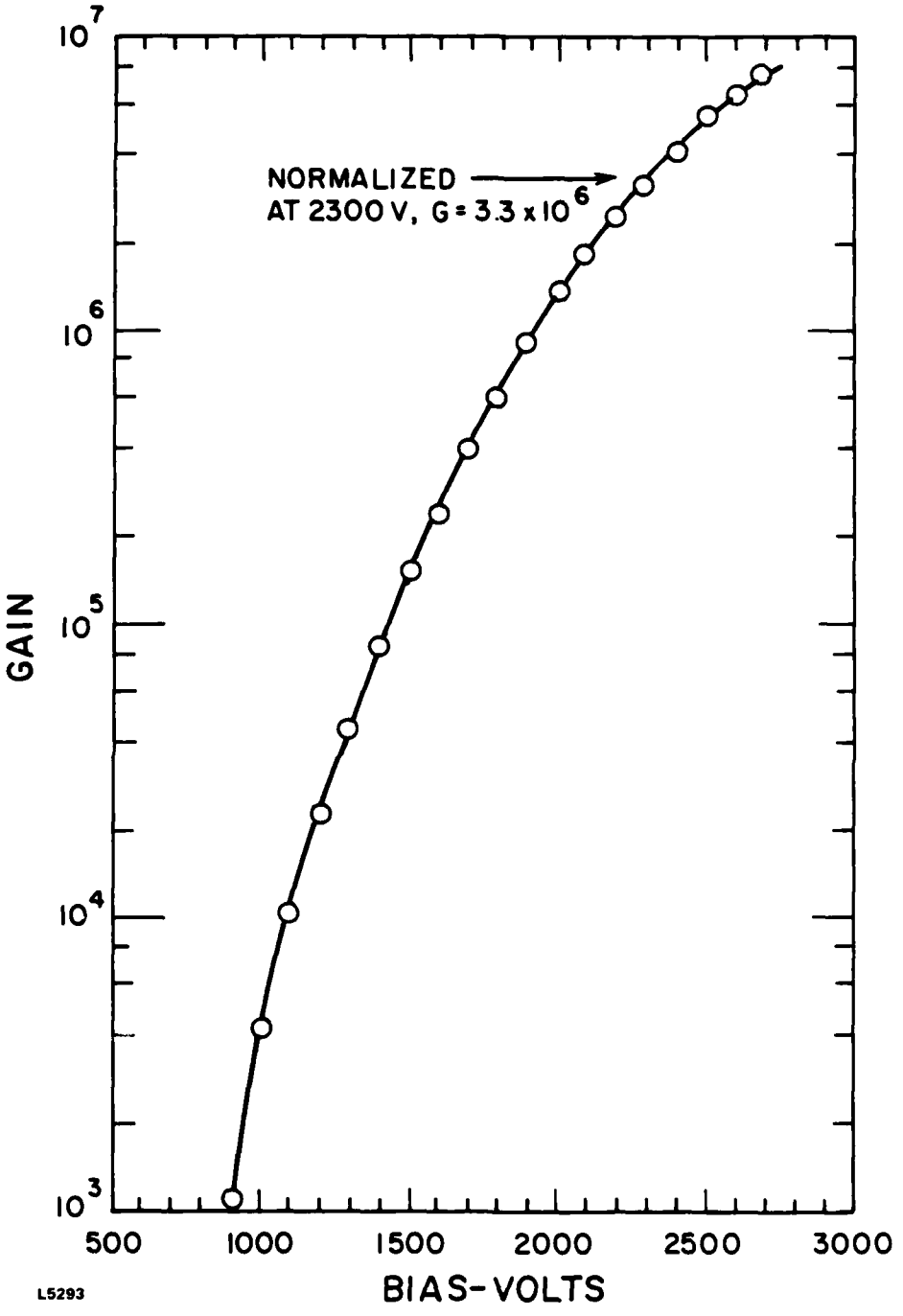


Figure 3 Measured Gain vs Voltage of the Channeltron, Calibrated Using Li^+ Ions.

In our Phase I work we estimated that the attachment of 1 in 10^4 electrons could be observed. With the introduction of the channeltron we enhanced this number to ~ 1 in 10^7.

1.2.3 Identification of Li^- Signals

Li^- signals were first observed at an oven temperature of ~ 700°C. The Li^- ions arrived as a sharply defined peak on the time-of-flight spectrum of negative ions, between features which were subsequently attributed to H^- and OH^-. A typical negative ion time-of-flight spectrum is shown in Figure 4. The delay between the leading edge of the extractor pulse and the Li^- peak was measured to be 1.6 μsec, identical to the Li^+ delay. When the detailed shape of the 2.1 kV extractor pulse was measured, it was shown to have a 200 nsec rise time, approximately flat top (of variable duration, usually 300 nsec), and decay time of 300 nsec. The pulse was applied between tungsten mesh screens of > 90 percent transmission, separated by 5 cm. The distance from the nearest mesh to the channeltron detector was 21 cm. At first it was difficult to assign the broad peak which arrived in front of the Li^- peak (Figure 4). However the most likely source of this peak is a burst of H^- ions released from the further mesh as it is struck by a large number of Li^+ ions travelling away from the channeltron. The predicted arrival time exactly matches the measured one, and surface production of H^- is well documented following the bombardment of tungsten by alkali metal ions. Only a monolayer of H atoms is required on the surface, or alternatively a LiH coverage might also have this effect. The arrival time cannot be accounted for by volume production of H^- or by charge exchange elsewhere in the flight tube. In addition to the H^- peak there is a later, broad peak of negative

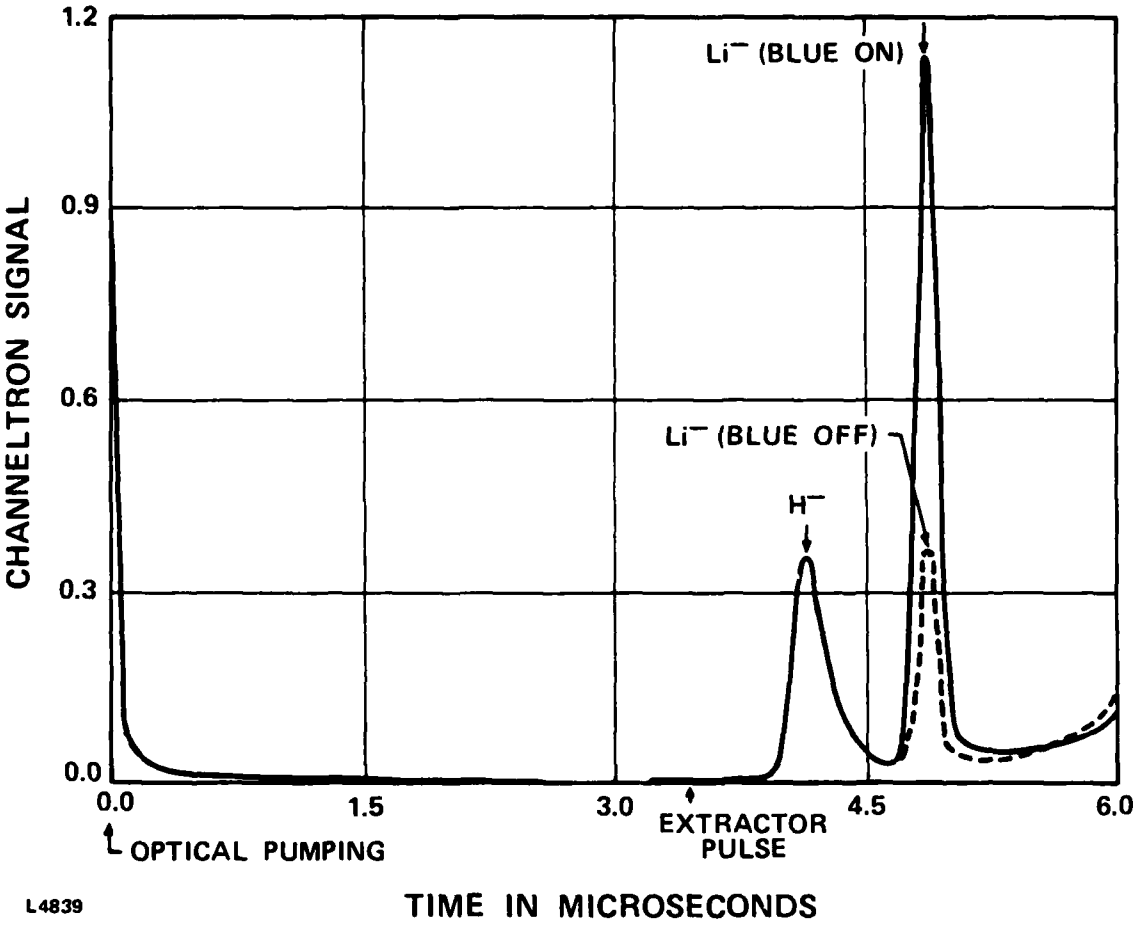


Figure 4 Time-of-Flight Negative Ion Spectrum for Optical Pumping on the Li_2 (B-X) 5-0 Band. Extractor delay 3.5 μsec.

species in the > 3 μsec delay region. Because of the breadth of this peak its assignment is difficult, but OH^- from the impact of Li^+ with the further mesh is a possible candidate.

Apart from the arrival time another indicator of the identity of the Li^- peak is the dependence of most of its amplitude on Li_2 (B-X) optical pumping (e.g., Figure 4). The signal amplitude is modulated as the pump laser is scanned through one of the Li_2 (B-X) vibrational bands, in a manner which resembles the expected degree of optical pumping. The detailed correlation of the Li^- signal with pumping on different rotational transitions has yet to be performed, but preliminary data indicates that there will probably not be any strong variation of attachment with rotational state. The fact that there is a part of the Li^- signal which is present even without blue pumping is interesting and will be given a more detailed discussion in a following section.

The strongest indication that the Li^- signal is due to a volume attachment process is its almost linear buildup in the several microseconds following optical pumping. This buildup of the integrated Li^- signal is plotted in Figure 5, in which the two components of the signal have been separated. (Li_2 (B-X) pumping is referred to by 'blue' as the bands of interest (v' = [1,7] - v" = 0) lie in that region of the spectrum). A linear signal increase is characteristic of volume attachment in which there is a partial 'reaction' of electrons with vibrationally excited $Li_2(X)$ molecules. This time dependence rules out any prompt mechanisms for Li^- production such as, for example, polar dissociation by the absorption of photons.

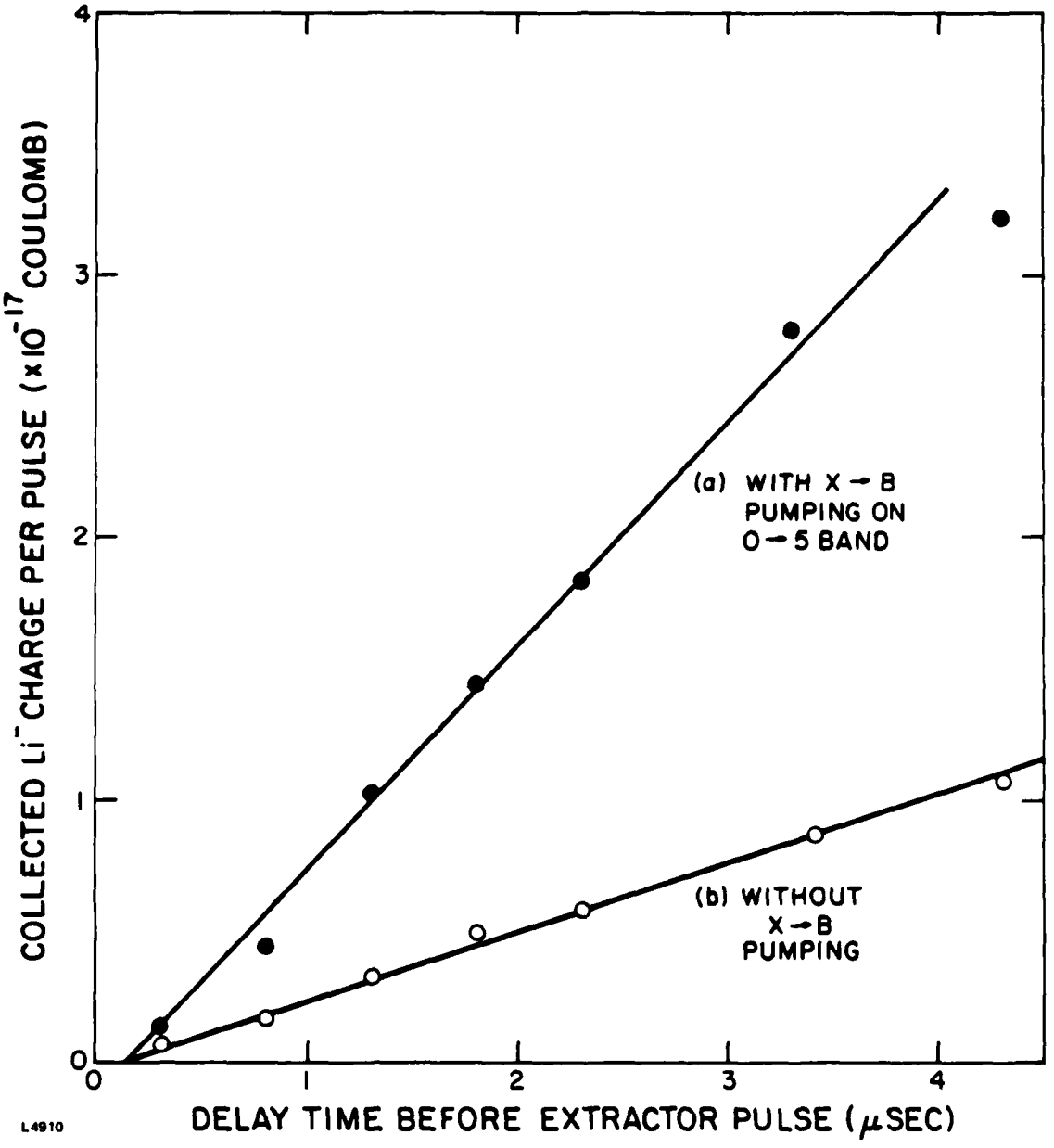


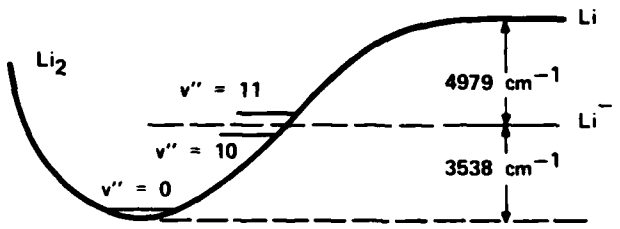
Figure 5 Integrated Li^- Signal vs Extractor Pulse Delay for Optical Pumping on the Li_2 (B-X) 5-0 Band.

Once observed, the optimization of Li^- signals has been relatively easy. It has been found that accurate alignment of the three pump laser beams is very important. Also, it is important to have a strong Li_2^+ signal which indicates that the beam rotational temperature is low (< 150°K). This signal is a measure of the accessible population in the Li_2 [X; v" = 0; J" = 0 → 5] rotational states. If, as has sometimes happened, there has been a higher than usual concentration of Li atoms in the beam path, the rotational heating has been sufficient to greatly reduce the signal. Such effects are thought to have caused the intermittent signals in Phase I which caused us to place a pessimistic upper bound on the attachment rate constant. The performance of the supersonic beam will be discussed below in more detail.

1.2.4 Vibrational Dependence of Attachment

We have measured the Li^- signal dependence on optical pumping to different $Li_2(B)$ vibrational states, including v_B = 4,5,6,7. Further work is planned on v_B = 2,3. Figure 6 indicates the distribution of Li_2 (X, v") states populated by optical decay from three of these v_B. Only about 40 percent of the Franck-Condon totals are listed in Figure 6, the remainder being to much lower vibrational states, as illustrated schematically in Figure 7, where the area of the dots is proportional to the Franck-Condon factor between the states concerned.

The threshold for attachment to Li_2 by 'zero' energy electrons lies between v" = 10 and v" = 11, as summarized in Figure 6. In the estimation of this threshold we have used the data of Verges et al,[8] for the well depth in Li_2 (8511 cm^{-1}) and the recent estimate of Peterson and al[9] for Li^- binding (4979 cm^{-1}).



FRANCK–CONDON FACTOR FOR DECAY OF UPPER LEVEL			TERMINAL LEVEL, ENERGY REL. TO Li_2 WELL BOTTOM		ATTACHMENT ENERGY EXCESS OR DEFECT (–)	
$v_B = 4$	$v_B = 5$	$v_B = 6$	v''	(cm^{-1})	(cm^{-1}) ≡	(eV)
0.14	0.02	0.07	7	2487	–1051	–0.130
0.20	0.06	0.08	8	2795	–743	–0.092
0.12	0.19	–	9	3098	–440	–0.055
0.04	0.16	0.14	10	3395	–143	–0.018
0.01	0.07	0.19	11	3687	149	0.018
–	0.02	0.11	12	3972	434	0.054
–	–	0.04	13	4251	713	0.088

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Figure 6 Energetics of Dissociative Attachment in Li_2, with Reference to Li_2 (B-X) Optical Decay into Li_2 (x,v").

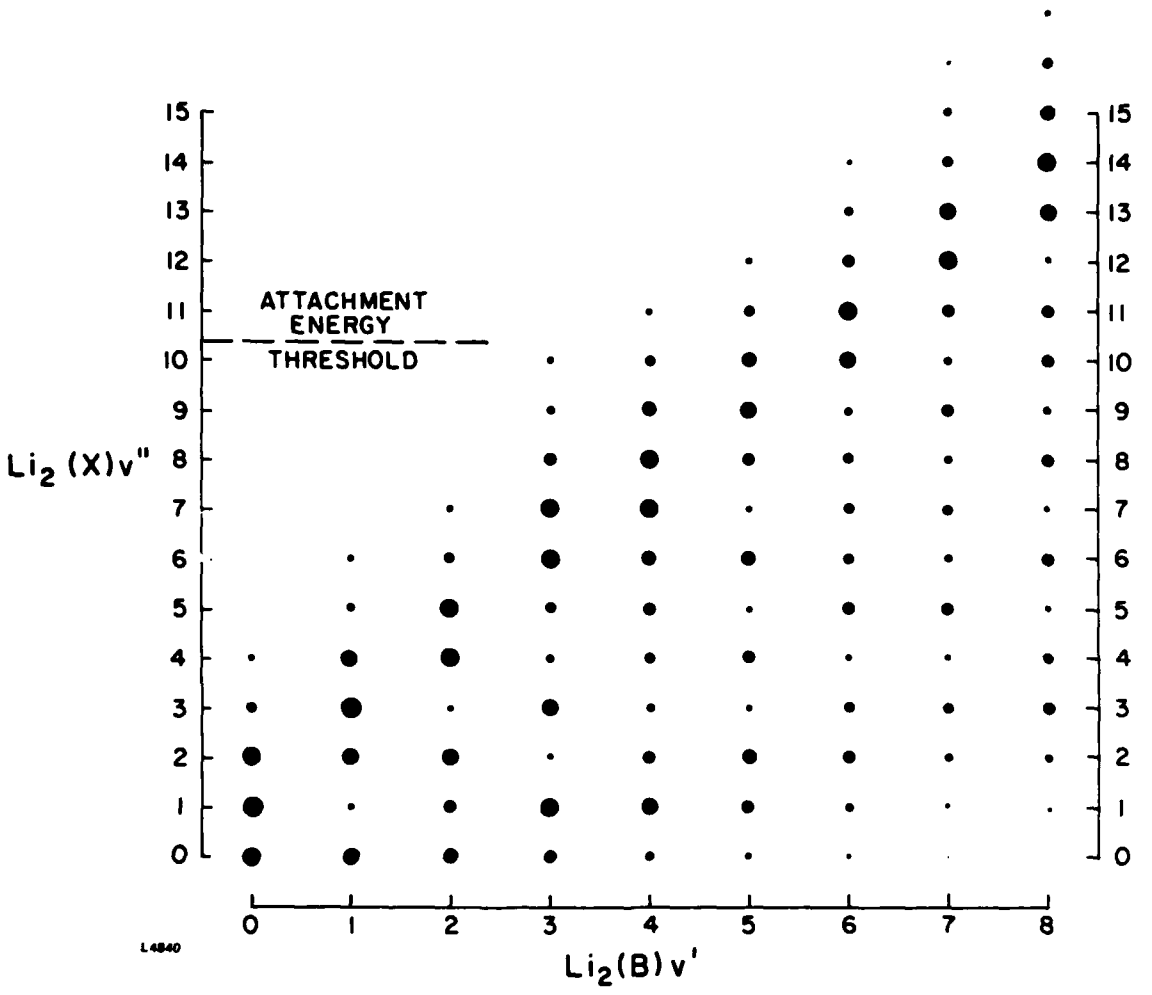

Figure 7 Visual Representation of Franck-Condon Factors for Li_2 (B-X) Optical Decay. Area of dot represents factor.

From Figure 6 we see that optical pumping to $v_B > 4$ would allow the attachment of electrons of 0.13 eV energy, such as those employed in the present experiment. Indeed, in our measurments we observed comparable Li^- signals for pumping on each of the bands $v_B = 4,5,6,7$. At the time of writing we do not have data for $v_B < 4$, but hope to gain this in the near future. The energetics would disallow attachment for most of the electrons in this case, so that we would predict a substantially decreased signal.

Since the Li_2 (B-X) pump transitions were locally saturated by the pump laser, each of the different intermediate levels $v_B = 4,5,6,7$ led to approximately equal population in its appropriate decay group of high vibrational states. We had previously verified[1,2] that a certain fraction of v" = o, $Li_2(X)$ molecules was removed by optical pumping, through a measurement of the reduction in Li_2^+ signal out of low J" states near the bandhead. This data was used to compute that 2.5 percent of the Li_2 molecular density was pumped into a usable group of high Li_2 (X,v") levels. The Li_2 fraction in the beam was estimated to be 4 (± 1) percent[10] in this experiment, and the Li density at 760°C was ~ 1×10^{13} cm^{-3},[1] so that the attacher density in each case was 1×10^{10} cm^{-3}.

Calibration of the Li^- signal as a fraction of the Li^+ signal (on the assumption of equal channeltron sensitivity, discussed above) lead to the attachment rate constant estimate of 3×10^{-8} cm^3 sec^{-1} for each of the groupings pumped via $v_B = 4,5,6$ and 7. The accuracy of this rate constant is only to within a factor of 2 or 3, given all the separate measurements which go into it. More detailed work is proposed in the continuation which should decrease the error somewhat, and possibly show up differences in the attachment with vibrational state which cannot be resolved at present.

This same attachment rate constant of 3×10^{-8} cm^3 sec^{-1} applies to all the v" groupings [7,8,9], [9,10], [10,11,12] and [12,13] obtained by pumping v_B = 4,5,6 and 7 respectively (Figure 6). All these combinations have excess energy for incident electrons of 0.13 eV energy, and their similarily in attachment is consistent with there being a bound Li_2^- channel, as illustrated in Figure 8. In fact a preliminary estimate[11] of the width of the Li_2^- resonance in the autodetaching region indicates that it may have a sufficiently long life to survive for more than one vibrational period, and hence give the observed high attachment rate due to the lack of a large autodetachment loss.

1.2.5 The Li^- Background Signal

As shown in Figures 4 and 5 there is also a component of the Li^- signal which does not depend on optical pumping. Such a component must depend for its existence upon some other source of Li_2 (X, v" > 7) molecules, because of the attachment energetics. There are two candidates for this source, between which unfortunately we cannot distinguish without further experiments: (a) Optical pumping on the Li_2 [A (v' = 5) - X (v" = 1)] band by the Li resonance photon at 671 nm, used for photoionization, and (b) formation of vibrationally 'hot' dimers in the expansion just downstream of the slit nozzle. It is possible that both of these effects contribute to the active Li_2 (v") population.

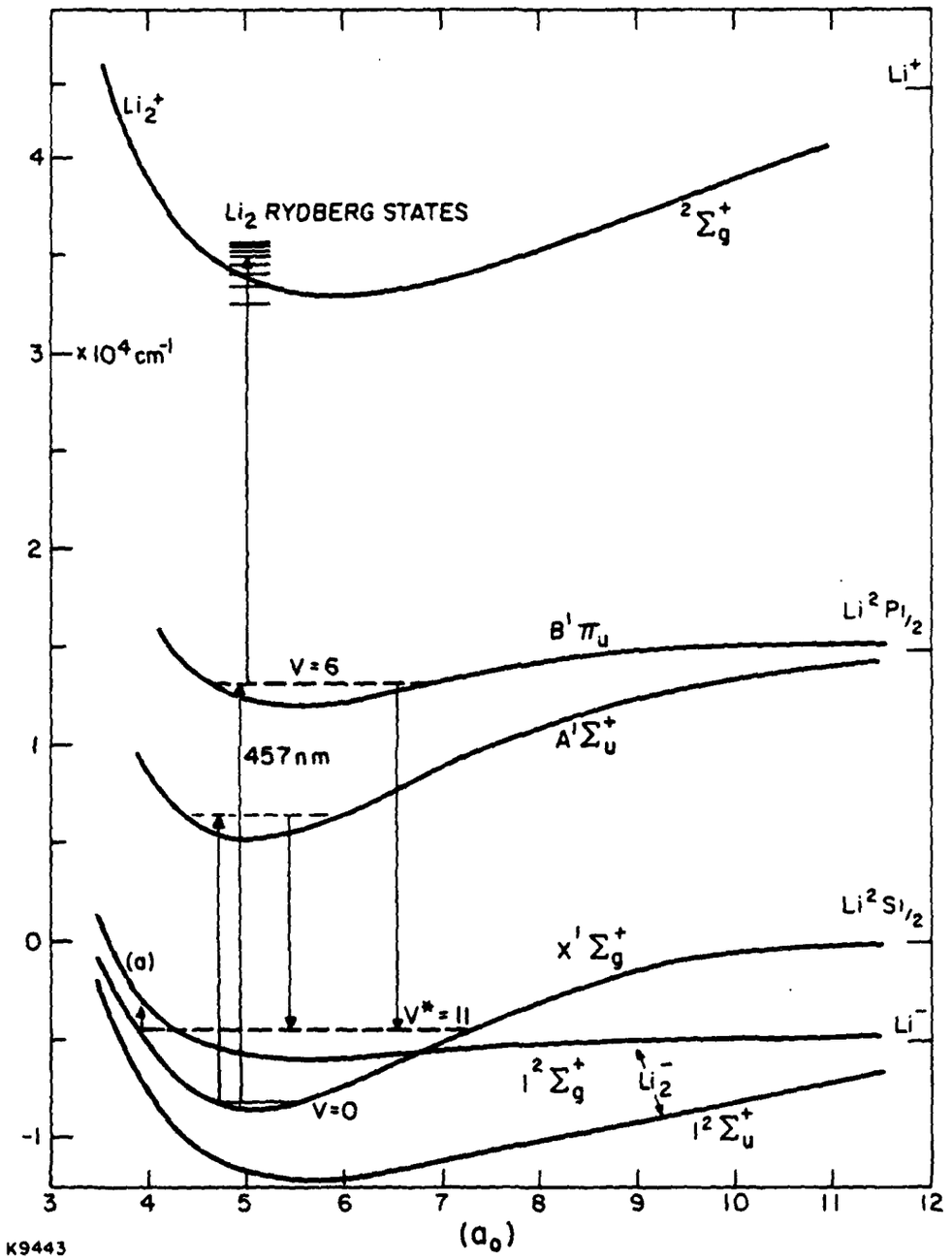

Figure 8 Potential Energy Diagram for Li_2, Li_2^- and Li_2^+, Showing the Li_2 $1^2\Sigma g^+$ Attachment Channel.

With regard to (a), the vibrational population of Li_2 (X, v" = 1) has not been measured in our past work, although evidence has been seen of Li_2^+ formation out of v" = 1,2 in the course of our other studies. It is possible that a significant fraction of Li_2 molecules are in the v" = 1 level, because vibrational relaxation typically freezes out at a higher temperature than rotational relaxation in supersonic expansions.[12] Evidence of this has been obtained in the case of sodium[13] for which T_v = 153°K and T_r = 55°K, and also for lithium[14] for which T_v = 195°K and T_r = 70°K, both of these results referring to the rapid cooling obtained in expansions from circular nozzles. If we assume that our measured slit nozzle rotational temperature of 150°K is matched by a vibrational temperature of ~ 400°K, then a v" = 1 fraction of 20 percent is possible. The Franck-Condon factor for the Li_2 [A(v' = 5) ← X(v" = 1)] transition is 0.068, much larger than that available for pumping the Li_2 [Li_2 B(v' = 5) ← X(v" = o)] transition, which is 0.013. Consequently, the saturation bandwidth is extended by several times in the A-X pumping case, relative to the B-X case, depending on the spectral profile of the pump laser. The radiative decay from the Li_2 (A, v' = 5) state is mainly to v" = 11,12, which have excess energy for attachment. It is therefore plausible to attribute the Li^- background signal to inadvertent A-X optical pumping at 670.96 nm (the Li 2s-2p wavelength) which coincides exactly with the bandhead of the Li_2 [A(v' = 5) ← X(v" = 1)] transition (actual head 670.86 nm, shaded to red). This hypothesis could be confirmed by the optical removal of population from the Li_2 (X,v" = 1) rotational states J" = 0 → 10 which contribute to absorption near the bandhead.

With regard to (b) there is some doubt as to the final vibrational state of dimers formed in the downstream expansion. It is the opinion of Gordon et al.,[12] that about 60 percent of the chemical energy released in the recombination of two lithium atoms to form Li_2 remains as vibrational excitation of Li_2 in such expansions, whereas Sinha et al.,[13] say that they do not see any evidence of 'hot' dimers in a spectroscopic study. In our own work we have seen some not very conclusive evidence of 'hot' dimers, and we incline to the view that there are indeed hot dimers present but that they are difficult to see spectroscopically because, having been formed late in the expansion, they have not cooled rotationally, and therefore do not display a prominant bandhead. Because of the importance of the beam dimer content for source work we are proposing to re-visit this subject in a continued program. For the present we note that the 'hot' dimer content of the beam can theoretically be large enough to explain the Li^- background signal without invoking optical pumping. The ground state Li_2 manifold has 30 vibrational levels, 70 percent of which have enough energy to attach low energy electrons. In our expansion we estimate, using the analysis of Gordon et al.,[12] that the dimer content of the beam is enhanced by about 1.8 percent in passing through the nozzle over the 3.1 percent in the oven at 760°C and that the dimer content is enhanced by another 0.5 percent downstream. The fraction of 'hot' dimers available for attachment is therefore crudely ~ 4 percent. As we noted above the Li^- signal due to (B-X) pumping was accounted for by only 2.5 percent of the dimers having been pumped to high vibrational states, so that the 'hot' dimer hypothesis for the background signal is also plausible. Further measurements on the hot dimer content would help to clarify this point.

1.2.6 Performance of the Li Supersonic Beam

We have encountered difficulties this year in the use of the lithium supersonic beam apparatus, which were not present in our first year of work. Recently we have diagnosed that the lower part of the condensing skimmer has been responsible for a part of the difficulty, in that it has been tending to run cooler than originally intended (about 220°C vs 300°C) consequently rendering the return flow of lithium viscous, and probably leading to lithium droplets falling onto the hot slit plate on top of the crucible. When a droplet falls on the slit plate the resulting increase of lithium vapor pressure heats the Li_2 molecules rotationally, but does not impede the main Li atom flow. Rotational heating has a devastating effect on the efficiency of optical pumping, however, and may readily be seen in a decreased Li_2^+ signal at the bandhead. The skimmer temperature is set by thermal contact through a stainless steel plate to the cooling water, and it is believed that periodic dis- and re-assembly of the beam apparatus has gradually led to improved thermal contact at a joint in the structure, thereby leading to the gradual development of this problem. Another possible change that could be occurring is a decrease in the 'wettability' of the condensing skimmer surface (304 stainless steel) due to some as yet unknown chemical ageing process. This is not thought to be too likely in view of the clean appearance of the skimmer surface, and could in any case be tackled by re-machining the surface to expose fresh steel.

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